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PATENT SPECIFICATION

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1 466 799

- (21) Application No. 16919/74 (22) Filed 18 April 1974
- (31) Convention Application No. 67482
- (32) Filed 20 April 1973
- (31) Convention Application No. 68831
- (32) Filed 19 Nov. 1973 in
- (33) Luxembourg (LU)
- (44) Complete Specification published 9 March 1977
- (51) INT CL² C01B 15/00; C11D 3/60 (C11D 3/60, 3/04, 3/39)
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(54) PARTICULATE PEROXYGEN COMPOUNDS

(71) We, INTEROX, of 33 Rue Prince Albert, 1050 Brussels, Belgium, a body corporate, organised and existing under the laws of Belgium, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to particulate peroxygen compounds stabilised by coating, to a coating process therefor and to detergent mixtures containing such compounds.

It is well known that peroxygen compounds can be employed as bleaching compounds in powder detergent mixtures. Sodium perborate tetrahydrate is usually employed as a bleaching compound in the standard domestic detergents because it is comparatively stable to decomposition in a detergent medium. However, the practice of using cold laundry washing and steeping techniques is becoming increasingly widespread. Under such conditions, sodium perborate suffers from the disadvantage of dissolving too slowly at 20°C.

It has been suggested that one way of overcoming this disadvantage is to use detergent

sium sulphate heptahydrate. In this case, comparatively large proportions of coating agents must be used in order to ensure adequate stability and the granules of stored material show a partial tendency to agglomeration.

According to the present invention there is provided a particulate composition comprising an alkali metal persalt selected from alkali metal percarbonates, perpyrophosphates, pertripolyphosphates, persilicates and peroxy-monosulphates, coated with a mixed salt comprising sodium carbonate and a compatible sodium salt.

In another aspect of the present invention there is provided a process for at least partially stabilising an alkali metal persalt selected from alkali metal percarbonates, perpyrophosphates, pertripolyphosphates, persilicates and peroxy-monosulphates to decomposition comprising coating the persalt with a mixed salt comprising sodium carbonate and a compatible sodium salt. Suitably the compatible sodium salt is sodium sulphate or sodium carbonate, the mixed salt preferably being sesquicarbonate. Desirably the mixed salt of sodium sul-

ERRATA

SPECIFICATION No. 1,466,799

Page 6, line 61, *for* metal carbonates *read* metal percarbonates
 Page 6, line 63, *after* comprising *insert* coating the persalt with a mixed salt comprising sodium

THE PATENT OFFICE
 7th August, 1978

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 G1D74 G1D75 G50 G50D34
 C5D 6A2 6A5B 6A5C 6A5D2 6A5E 6A8C 6B12B1
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It is well known that peroxygen compounds can be employed as bleaching compounds in powder detergent mixtures. Sodium perborate tetrahydrate is usually employed as a bleaching compound in the standard domestic detergents because it is comparatively stable to decomposition in a detergent medium. However, the practice of using cold laundry washing and steeping techniques is becoming increasingly widespread. Under such conditions, sodium perborate suffers from the disadvantage of dissolving too slowly at 20°C.

It has been suggested that one way of overcoming this disadvantage is to use detergent powders admixed with many other inorganic peroxygen compounds, particularly the percarbonates, perphosphates and peroxy monosulphates of alkali metals, which have suitable dissolution rates. The said peroxygen compounds, particularly the percarbonates, decompose too rapidly, particularly when they are stored in a moist atmosphere. In addition, the other ingredients of the cleaning composition may even trigger decomposition. One method which has been suggested as a way of avoiding this defect involves coating peroxygen compounds with stabilising substances or protective inorganic films, for example a sodium silicate solution (A. Welter—Br. Pat. 174891 of 26.7.1920) or certain magnesium salts, for example magne-

sium sulphate heptahydrate. In this case, comparatively large proportions of coating agents must be used in order to ensure adequate stability and the granules of stored material show a partial tendency to agglomeration.

According to the present invention there is provided a particulate composition comprising an alkali metal persalt selected from alkali metal percarbonates, perpyrophosphates, pertripolyphosphates, persilicates and peroxy-monosulphates, coated with a mixed salt comprising sodium carbonate and a compatible sodium salt.

In another aspect of the present invention there is provided a process for at least partially stabilising an alkali metal persalt selected from alkali metal percarbonates, perpyrophosphates, pertripolyphosphates, persilicates and peroxy-monosulphates to decomposition comprising coating the persalt with a mixed salt comprising sodium carbonate and a compatible sodium salt. Suitably the compatible sodium salt is sodium sulphate or sodium carbonate, the mixed salt preferably being sesquicarbonate. Desirably the mixed salt of sodium sulphate and sodium carbonate has the general formula $\text{Na}_2\text{SO}_4 \cdot n\text{Na}_2\text{CO}_3$ wherein n is from 0.3 to 3 and preferably n is from 0.5 to 1.1.

In a further aspect of the invention there is provided a process for coating the persalts with the mixed salt comprising depositing the mixed salt onto the persalt from a solution containing the constituent parts of the mixed salt in appropriate proportions and at a temperature conducive to the formation of the mixed salt.

Suitable alkali metal persalts which are normally unstable to water induced a decomposition on storage, and which advantageously may be coated according to the present invention, are preferably the percarbonates, perpyrophosphates, pertripolyphosphates, and peroxy-monosulphates.

Typically sodium percarbonate can be coated extremely successfully using a process according to the present invention.

Advantageously the coating comprises from 5 0.5% to 20% by weight based on the persalt. An amount of 0.5% by weight is sufficient to ensure at least partial coating and improved stabilisation of the peroxygen compound, and it is unnecessary to use more than 20% by 10 weight to ensure a complete coating. A convenient amount is from 3 to 15% by weight of coating agent, based on the persalt.

Desirably peroxygen compounds according to the present invention may be used in washing or bleaching compositions. Other standard 15 components may be included in such compositions, for example bleaching activators, anionic or non-ionic surfactants, builders, such as carbonates, phosphates, pyrophosphates, tri- 20 polyphosphates, silicates, antiredispersion agents such as carboxymethyl - cellulose, optical bleaching agents, proteolytic and/or amylolytic enzymes, stabilizers, anti-corrosion agents and the like. Suitable anionic or non- 25 ionic surfactants include those described by Z. P. Sisley and P. I. Wood in "The Encyclopaedia of Surface Active Agents" published by Chemical Publishing Co., New York, Volume 1 in 1961 and in Volume II in 1964, 30 those in French Specification 1589887 and those in German Patent Specification 1594865.

In particular, in certain embodiments according to the present invention the peroxygen compound satisfies the following test, by 35 losing no more than 15% of active oxygen after four weeks in admixture with a base detergent i.e. a detergent powder which contains no peroxygen compound but does contain the other usual ingredients, in a sufficient 40 amount to provide 2% by weight of active oxygen in the mixture. The compositions of one such base detergent powder is shown in Table 2 herein. Storage of the mixture is conducted at 28°C and a relative humidity of 70% in cardboard boxes sealed internally 45 and externally by a film of cellulose acetate.

Coating of the persalt particles may be carried out using any recognised means, and the method employed is not critical but one 50 preferred technique comprises spraying an aqueous solution of sodium carbonate, containing in addition either sodium bicarbonate or sodium sulphate onto moving particles of the persalt, and evaporating off water at a 55 temperature conducive to formation of a mixed salt, and thereby depositing the mixed salt on the surface of the persalt.

When the mixed salt is to be sodium sesquicarbonate or a sodium sulphate/sodium carbonate mixed salt the temperature of the 60 solution from which the mixed salt is deposited should be maintained at between 30°C and 80°C. The nature of the mixed salt will also depend of course on the mole ratio of 65 the constituents of the mixed salt and can be

seen from the phase diagrams of the system. In the case of the sodium carbonate/sodium bicarbonate/water system, the information is available in Kirk Othmer "Encyclopaedia of Chemical Technology" Volume 17 Second 70 Edition, on page 466.

Apparatus in which moving persalt particles may be sprayed, suitably comprises a fluidised bed, a rotary hearth, a rotary drum or other 75 similar recognised devices. It is preferred to use a fluidised bed because a more hermetic and more homogenous coating generally results, all other conditions of coating being equal, thereby resulting in less coating agent 80 being required to stabilise the persalt particles to a given extent, and thus reducing the amount of solvent, usually water, which must be removed by evaporation. Coating using a fluidised bed may be carried out continuously or batch-wise. If a continuous coating method 85 is used the fluidised bed should preferably be compartmented. Product can be removed from one compartment of such a bed by simply overflowing, or by elutriation via a pipe located at any desired level in the bed. The tempera- 90 ture at which simultaneously the persalt is coated, and solvent is evaporated off is of course controlled at below the decomposition temperature of the persalt. Naturally the decomposition temperature will vary according 95 to the identity of the persalt, but in general the limit may be set at 100°C. However, in the case of sodium percarbonate, which is a comparatively heat sensitive product, it is preferred not to exceed approximately 80°C. 100

Certain embodiments of the present invention will now be described more fully by way of example. Examples 3, 4, 5 and 8 are according 105 to the present invention. Examples 6 and 7, which describe coating using respectively solely sodium carbonate or sodium sulphate, and Examples 1 and 2 employing respectively uncoated sodium percarbonate and uncoated sodium perborate are present for purposes of 110 comparison only.

In Examples 3 to 8 sodium perborate was coated using a batchwise process in a fluidised bed.

The apparatus used consisted of a cylinder of 15 cm diameter and 77 cm height, fitted 115 at its base with a gas distributor plate pierced with holes of 2 mm diameter, and provided with a pipe bundle for heating using steam maintained at an effective pressure of 1 kg/cm². 120

First of all the apparatus was charged with 3 kg of homogeneous sodium percarbonate granules. A stream of air was then passed through the gas distributor plate to fluidise the sodium percarbonate granules, and an 125 aqueous solution to form the appropriate coating agent was sprayed onto the granules through a pneumatic spray located on the wall of the cylinder 11 cms above its base. When introduction of the solution had been com- 130

pleted, and the coated persalt granules dried, the granules were then removed from the apparatus.

The operating conditions for each Example, are summarised in Table 1 herein below.

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TABLE I

Coating Conditions	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
Rate of flow of fluidising gas, m ³ N/h	38	37	38	31	32	31
Input temperature of fluidising gas, °C	80	102	83	120	120	120
Duration of spraying with solution, minutes	35	40	30	30	30	30
Amount of solution introduced, kg	0,47	0,94	0,48	0,60	0,60	0,75
Concentration in the solution in g/kg						
of Na ₂ SO ₄	180	180	228	—	250	—
of Na ₂ CO ₃	140	140	85	250	—	172
of NaHCO ₃	—	—	—	—	—	50
Mole ratio Na ₂ CO ₃ /Na ₂ SO ₄	1,04	1,04	0,5	—	—	—
Mole ratio Na ₂ CO ₃ /NaHCO ₃	—	—	—	—	—	2,27
Weight ratio of coating agent to persalt, g/100 g	5	10	5	5	5	5
Fluidised bed Temperature °C	50	50	52	60	60	50
<u>Properties of Coated Percarbonate</u>						
Mean diameter of the granules mm	0,42	0,39	0,42	0,415	0,41	0,41
Free flowing density kg/dm ³	1,20	1,15	1,22	1,21	1,19	1,20
Active oxygen content g/kg	134	131	135	135	135	134

Shelf Tests

The following tests were carried out to evaluate the effectiveness of coating percarbonate according to the present invention.

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a) Shelf test in small boxes

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In this test mixtures were used which contained approximately 2% of active oxygen comprising 7 g of sodium percarbonate (uncoated or coated) or 10.5 g of sodium perborate (uncoated) and 42 g of a commercial

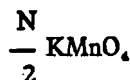
persalt-free base detergent powder either with or without enzymes having compositions given in Table 2. After homogenisation, the mixtures were placed in cardboard boxes (11.5×7×2 cm) lined on both sides with a cellulose acetate film resulting in a permeability by water of 550 g/m².day. The filled boxes were then stored at 28°C at 70% relative humidity for 4, 8 and 12 weeks respectively. In a second series of tests further portions of the mixtures were placed in similarly sized boxes

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which had been coated with a microcrystalline wax, to give a permeability by water of 5 g/m²/day. These boxes were stored at 35°C and 80% relative humidity for 4 to 8 weeks.

- 5 After each storage period, the active oxygen content of the powder was determined by direct titration with



- 10 and the active oxygen loss relative to the original active oxygen evaluated. The percentage active oxygen loss of the coated sodium percarbonate was compared with the percentage active oxygen loss of the uncoated sodium percarbonate and of the sodium perborate (staple product taken as reference) prepared under the same test conditions. The results are expressed in terms of the formula:

$$\frac{\text{TPCS uncoated} - \text{TPCS coated}}{\text{TPCS uncoated} - \text{TPBS uncoated}} \times 100 = x\%$$

- 20 in which "T" represented the "active oxygen loss," "PAS" sodium perborate and "PCS" sodium percarbonate. They showed the percentage improvement in the stability of sodium percarbonate attributable to coating in relation to the stability of uncoated sodium perborate which was taken as a reference because most consumers felt it to be adequate.
- 25 The active oxygen content was measured by

introducing approx. 10 g of washing powder weighed to the nearest 0.01 g in a 750 cc capacity "Erlenmeyer" flask, adding 100 cc of 6N H₂SO₄, 100 cc of distilled water and 2 drops of silicone anti-foaming agent. The mixture was then shaken until such time as a homogeneous solution was obtained and then titrated with N/2 KMnO₄ until a pink colouration lasting 30 sec. was obtained. A blank test was also performed on an equivalent amount of washing powder not containing persalt. The active oxygen content of the specimen, O, expressed in g of oxygen/kg was given by the relationship

$$O = (a - b) \times \frac{1}{2} \times \frac{1000}{P} \times \frac{0.016}{2}$$

in which

—a, cm³, denoted the volume of N/2 KMnO₄ used for titrating the powder containing persalt

—b, cm³, denoted the volume of N/2 KMnO₄ used for the blank titration

—p, g, denoting the weight of sample employed.

The results of the foregoing shelf tests are summarised in the following Tables 3 and 4. These results clearly point to the superiority of stability to decomposition of percarbonate coated with a mixed salt according to the present invention, in comparison with uncoated percarbonate, or percarbonate coated with only sodium carbonate or sodium sulphate.

TABLE 2.

Commercial Powder used in Shelf Tests	Without Enzymes	With Enzymes
Sodium alkylarylsulphonate, g/100 g	24	29
Phosphates — Na ₅ P ₃ O ₁₀ (*) ..	43	29
Silicates — Na ₂ O.2SiO ₂ (**) ..	9	7
Na ₂ SO ₄ ..	12	25
H ₂ O ..	12	9
Enzymes D.U./g	—	850
(*) total P ₂ O ₅ expressed in terms of Na ₅ P ₃ O ₁₀		
(**) total SiO ₂ expressed in terms of Na ₂ O.2SiO ₂		

In Tables 3 and 4 the persalt is sodium percarbonate unless otherwise stated.

TABLE 3

Results of Shelf Tests using Enzyme-Free Detergents						
Coating of Persalt	Ex. No.	% Active Oxygen Loss / % improvement in stability				
		at 28°C and 70% RH.			at 35°C and 80% RH.	
		4	8	12	4	8
Uncoated	1	13/—	15/—	23/—	17/—	25/—
Uncoated Sodium Perborate	2	0/—	1/—	2/—	4/—	6/—
Na ₂ SO ₄ . 1.04Na ₂ CO ₃	3	3/77	11/29	17/29	0/131	8/87
Na ₂ SO ₄ . 1.04Na ₂ CO ₃	4	3/77	10/36	16/33	6/85	13/63
Na ₂ SO ₄ . 0.5 Na ₂ CO ₃	5	6/54	12/21		7/77	13/63
Na ₂ CO ₃	6	7/46	13/14		10/54	16/47
Na ₂ SO ₄	7	7/46			11/46	17/42
NaHCO ₃ . Na ₂ CO ₃	8	5/62				

TABLE 4

Results of Shelf Tests using Detergents containing Enzymes						
Coating of Persalt	Ex. No.	% Active Oxygen Loss / % improvement in stability				
		at 28°C and 70% RH.			at 35°C and 80% RH.	
		4	8	12	4	8
Uncoated	1	40/—	75/—	88/—	37/—	57/—
Uncoated Sodium Perborate	2	5/—	10/—	32/—	4/—	9/—
Na ₂ SO ₄ . 1.04Na ₂ CO ₃	3	13/77	41/52	54/61	1/109	12/94
Na ₂ SO ₄ . 1.04Na ₂ CO ₃	4	14/74	35/62	47/73	7/91	16/85
Na ₂ SO ₄ . 0.5 Na ₂ CO ₃	5	15/71	36/60	56/57	8/88	16/85
Na ₂ CO ₃	6	12/80	44/48	58/54	14/70	30/56
Na ₂ SO ₄	7	13/77	46/44	61/48	14/70	31/54

b) Shelf tests in commercial boxes

5 In this test mixture were prepared which contained 3.3% by weight of active oxygen, by mixing 94 grams of uncoated sodium percarbonate having an active oxygen content of 140 g/kg, or 98.5 grams of sodium percarbon-

ate coated with sodium sesquicarbonate having an active oxygen content of 134 g/kg with enough persalt-free enzyme-free base detergent powder having the composition shown in Table 2 to make up to 400 grams.

After homogenisation the mixtures were

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placed in carboard boxes of dimensions 20×14×5.5 cm which had been treated under heat with a micro-crystalline wax. The boxes were then stored at 20° or 35°C and at atmosphere of 80% relative humidity for 2, 4 and 8 weeks, and the tests were carried out in triplicate.

At the end of the selected storage period the active oxygen content of each mixture was measured by titration of a known amount of mixture dissolved in a known volume of water, against N/10 KMnO₄. The active oxygen Run in Table 5 following, is expressed as a percentage of the active oxygen present in the mixture before storage.

In more detail the method of measuring the active oxygen content comprised with-drawing a representative sample of 10—20 g, weighed to the nearest 0.01 g—(P grams)—and 50 ml of 60% H₂SO₄ dissolved in 1 litre of distilled water 57°C±2°C in a 2 litre beaker. The contents were stirred using a one inch SILVERSON LR2 bearing the mark immersed to a depth of 1 cm from the bottom of the beaker, and being rotated at

top speed. "SILVERSON" is a Registered Trade Mark. When the temperature of the solution had fallen to 48—52°C, the weighed sample was added. Stirring continued for 1 minute or longer until all the sample was dissolved. The solution was allowed to stand for 30 seconds to allow deaeration, and 50 ml was transferred to a 250 ml Erlenmeyer flask, and stirred vigorously against standardised N/10 KMnO₄. The amount of KMnO₄ solution (T mls) required to reach the end point, a pink colouration lasting at least 15 seconds after addition of 1 more drop of KMnO₄ was noted. The active oxygen content of the mixture was then expressed using the general formula

$$\% \text{ active oxygen} = \frac{TN}{P} \times \frac{0.8 \times 1050}{50}$$

wherein N is the actual normality of the KMnO₄ solution.

The results of the tests are summarised in Table 5.

TABLE 5

Results of Shelf Tests in Boxes of Commercial Design						
Coating	% active oxygen lost during storage at 20°C and 80% relative humidity					
	2 wks	4 wks	8 wks	2 wks	4 wks	8 wks
Uncoated	—	5.1	6.4	8.5	9.7	18.1
5% of sodium sesquicarbonate	—	5.0	5.6	5	5.4	12.3

These results clearly show the superiority of the products of the invention over the uncoated percarbonate.

WHAT WE CLAIM IS:—

1. A particulate composition comprising an alkali metal persalt selected from alkali metal percarbonates, perpyrophosphates, pertripolyphosphates, persilicates and peroxymonosulphates, coated with a mixed salt comprising sodium carbonate and a compatible sodium salt.

2. A process for at least partially stabilising an alkali metal persalt selected from alkali metalcarbonates, perpyrophosphates, pertripolyphosphates, persilicates and peroxymonosulphates, to decomposition comprising sodium carbonate and a compatible sodium salt.

3. A compound or process as claimed in claim 1 or 2 wherein the compatible sodium salt is sodium bicarbonate.

4. A compound or process as claimed in

claim 3 wherein the mixed salt is sodium sesquicarbonate.

5. A compound or process as claimed in claim 1 or 2 wherein the compatible sodium salt is sodium sulphate.

6. A compound or process as claimed in claim 5 wherein the mixed salt has the general formula Na₂SO₄.nNa₂CO₃ wherein n is from 0.3 to 3.

7. A compound or process as claimed in claim 6 wherein n is from 0.5 to 1.1.

8. A compound or process as claimed in any preceding claim wherein the persalt is an alkali metal percarbonate, perpyrophosphate, pertripolyphosphate or peroxymonosulphate.

9. A compound or process as claimed in claim 8 wherein the persalt is sodium percarbonate.

10. A compound or process as claimed in any preceding claim wherein the coating comprises from 0.5 to 20% by weight of the persalt.

11. A compound or process as claimed in claim 10 wherein the coating comprises from 3 to 15% by weight of the persalt. 20
12. A process for coating the persalt with the mixed salt as claimed in any of claims 2 to 11 comprising depositing the mixed salt onto the persalt from a solution containing the constituent parts of the mixed salt in appropriate proportions and at a temperature conducive to the formation of the mixed salt. 25
13. A process as claimed in claim 12 wherein the mixed salt is sesquicarbonate formed by evaporation of water from an aqueous solution of sodium carbonate and sodium bicarbonate at a temperature of from 30° to 80°C in a fluidised bed. 30
14. A process as claimed in claim 12 wherein the mixed salt is formed by evaporation of water from an aqueous solution of sodium carbonate and sodium sulphate in a mole ratio of from 0.3:1 to 3.0:1 at a temperature of from 30 to 80°C in a fluidised bed. 35
15. A process at least partly stabilising a persalt substantially as described herein with reference to any one of Examples 3, 4, 5 and 8.
16. A coated persalt whenever produced by a process claimed in any one of claims 2 to 15.
17. A coated persalt substantially as described herein with reference to any one of Examples 3, 4, 5 and 8.
18. Detergents containing a coated persalt according to any one of claims 1, 3 to 11, 16 and 17.

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Agent for the Applicants.